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Estimation and Structural Effect on Physicochemical Properties of Alkylimidazolium-Based Ionic Liquids with Different Anions

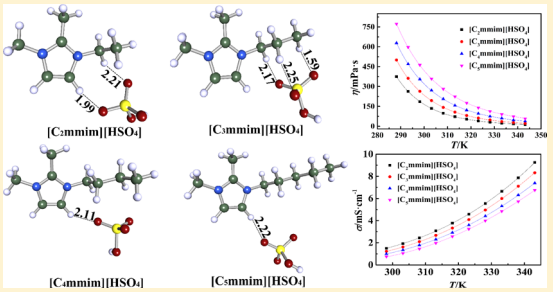
Qingguo Zhang,*[,†] Yalin Lan,[‡] Hongwei Liu,[§] Xinyuan Zhang,[‡] Xuelei Zhang,[‡] and Ying Wei[‡]

[†]College of New Energy, and [‡]College of Chemistry and Chemical Engineering, Bohai University, Jinzhou 121013, Liaoning Province, China

[§]Bureau of Environmental Supervision, Xishi District, Yingkou 115000, Liaoning Province, China

Supporting Information

ABSTRACT: Ten kinds of alkylimidazolium-based aprotic ionic liquids (AILs) with hydrogen carbonate, dihydrogen phosphate, and hydrogen sulfate anions were prepared, and methods of elemental analysis, infrared spectroscopy, and proton nuclear magnetic resonance were employed to characterize the ILs, respectively. Properties such as electrical conductivity, density, dynamic viscosity, surface tension, were measured and correlated with thermodynamic and empirical equations over various temperature ranges under ambient conditions. Some significant thermodynamic parameters of the ILs were estimated. The trends of changing with temperature for the dynamic viscosity and the electrical conductivity were described by the Vogel−Fulcher−Tamman equation. The activation energies of dynamic viscosity and electrical conductivity were also calculated. Further, the structures and the energetics of the ILs ions were obtained through combining density functional theory calculations and the COSMO-RS methodology. The structural effects of ion variation on the properties of the ILs were studied.



1. INTRODUCTION

As the unique physicochemical properties of ionic liquids (ILs),[1−8] more intensive investigations have been carried on in various fields, for example, the "green" solvents for specific organic reactions and extraction processes,[9−12] excellent electrolyte in various electrochemical applications,[13] the media of homogeneous catalysis,[14] and so on.

A subgroup of ILs, aprotic ionic liquids (AILs), has been widely investigated.[15−19] The cations most commonly used in AILs are alkylimidazolium with aromatic rings, in which the substitutions in positions 1 and 3 were alkyl groups, while the substitutions in positions 2, 4, and 5 were either hydrogen atoms or alkyl groups.[20] It is well-known that ILs could be tailored for particular purposes via specific cation−anion combinations. The AILs composed of alkylimidazolium cations and anions like hydrogen carbonate, dihydrogen phosphate, and hydrogen sulfate lack investigation by far, and these ILs may have potentials in certain industrial applications. For example, Zhang et al. used $[C_4mim][HSO_4]$ ionic liquid as a catalyst in oxidative desulfurization of dibenzothiophene, and in model oil, the IL catalyst was recyclable and showed high activity through the whole process of oxidative desulfurization of DBT.[14] Choib et al. reported that the IL $[C_4mim][HCO_3]$ had a comparable activity to $NaOCH_3$ and showed good potential to be a substitute for common alkali metal alkoxide and precious metal complexes.[21] The comprehensive evaluation of the physicochemical properties of these AILs will allow structure−property trends to be discussed, and for the development of industrial processes, the basic physicochemical data of ILs should be studied both experimentally and computationally to characterize the molecular structure and thermodynamic characteristics. In this context, the study of physicochemical properties, intermolecular interactions, structure characteristics, and the estimation of thermodynamic properties of these ILs become necessary in any of their applications.

Herein, we prepared three series of aprotic ionic liquids from alkylimidazolium cations and three anions, 1-alkyl-3-metylimidazolium hydrogen carbonate ($[C_{3-5}mim][HCO_3]$), 1-alkyl-3-metylimidazolium dihydrogen phosphate ($[C_{3-5}mim][H_2PO_4]$), and 1-alkyl-2,3-dimetylimidazolium hydrogen sulfate ($[C_{2-5}mmim][HSO_4]$) (see Table 1). A two-step method was employed and the prepared ILs were characterized by methods of IR, ^{1}HNMR, and EA. The physicochemical properties such as density, dynamic viscosity, surface tension, and conductivity were measured. The significant thermodynamic parameters of the ILs such as thermal expansion coefficient, lattice energy, standard molar entropy, and interstice parameters were estimated according to semiempirical/empirical methods. Subsequently, the temperature dependence of electrical conductivity and viscosity were described by the Vogel−Fulcher−Tamman (VFT) equation. Further, the structural effects on the properties of ILs, which resulted from the cation/anion size and position change of the alkyl chain of cations or

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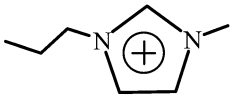
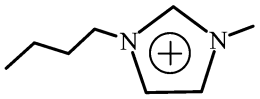
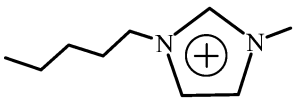
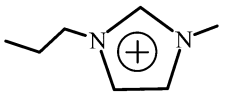
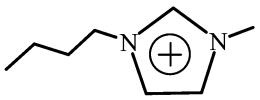
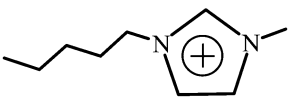
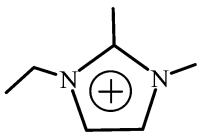
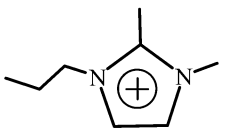
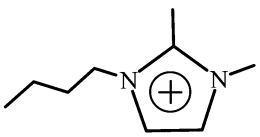
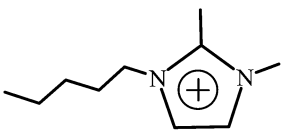
Table 1. Structure Formula of Synthetic Ionic Liquids

Ionic liquid	Abbreviations	Cation	Anion
1−propyl−3−methylimidazolium hydrogen carbonate	$[C_3mim][HCO_3]$		HCO_3^-
1−butyl−3−methylimidazolium hydrogen carbonate	$[C_4mim][HCO_3]$		
1−pentyl−3−methylimidazolium hydrogen carbonate	$[C_5mim][HCO_3]$		
1−propyl−3−methylimidazolium dihydrogen phosphate	$[C_3mim][H_2PO_4]$		$H_2PO_4^-$
1−butyl−3−methylimidazolium dihydrogen phosphate	$[C_4mim][H_2PO_4]$		
1−pentyl−3−methylimidazolium dihydrogen phosphate	$[C_5mim][H_2PO_4]$		
1−ethyl−2,3−dimetylimidazolium hydrogen sulfate	$[C_2mmim][HSO_4]$		HSO_4^-
1−propyl−2,3−dimetylimidazolium hydrogen sulfate	$[C_3mmim][HSO_4]$		
1−butyl−2,3−dimetylimidazolium hydrogen sulfate	$[C_4mmim][HSO_4]$		
1−pentyl−2,3−dimetylimidazolium hydrogen sulfate	$[C_5mmim][HSO_4]$		

different anions, were calculated and studied by DFT calculations and COSMO-RS methodology. The optimized energy models of the ILs were obtained by the calculation.

2. EXPERIMENTAL SECTION

2.1. Materials. Bromoethane, bromopropane, bromobutane, and bromopentane were purchased from Sinopharm Co., China, followed by distillation before use. Sodium hydrogen carbonate, sodium dihydrogen phosphate, sodium hydrogen sulfate were purified by recrystallization from water. The *N*-methyl imidazole and 1,2-dimethylimidazolium purchased from Zhejiang doubleport Co. Ltd., China, were distilled at reduced pressure before use. The materials' purities and sources were summarized in Table 2.

2.2. Preparation and Characterization of ILs $[C_{3-5}mim][HCO_3]$, $[C_{3-5}mim][H_2PO_4]$, $[C_{2-5}mmim][HSO_4]$. The ILs $[C_{3-5}mim][HCO_3]$, $[C_{3-5}mim][H_2PO_4]$, and $[C_{2-5}mmim][HSO_4]$ were prepared by a two-step method (see Scheme 1) according to previous work,[22,23] and then the viscous and transparent ionic liquids were obtained. All synthetic processes were conducted under dry argon atmosphere. These ILs were dried under high vacuum for 24 h at 353.15 K before use.

The ILs products were characterized by IR, ^{1}HNMR, and EA (see Supporting Information). A Karl Fischer moisture titrator

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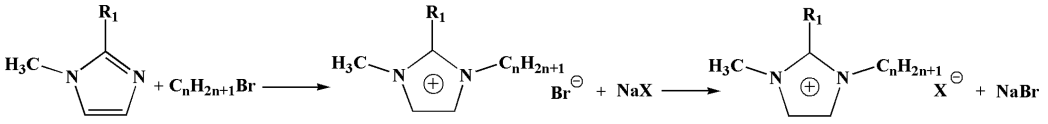
Table 2. Information of Sample and the Synthesized Ionic Liquids

chemical name	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
bromoethane	Sinopharm (China)	> 0.990	distillation	0.997	GC[a]
bromopropane	Sinopharm (China)	> 0.990	distillation	0.998	GC
bromobutane	Sinopharm (China)	> 0.990	distillation	0.996	GC
bromopentane	Sinopharm (China)	> 0.990	distillation	0.998	GC
sodium hydrogen carbonate	Sinopharm (China)	0.995	precipitation	> 0.995	
sodium dihydrogen phosphate	Sinopharm (China)	0.995	precipitation	> 0.995	
sodium hydrogen sulfate	Sinopharm (China)	0.995	precipitation	> 0.995	
N-methyl imidazole	Zhejiang doubleport (China)	> 0.990	distilled at reduced pressure	> 0.998	^{1}HNMR
1, 2-dimethylimidazolium	Zhejiang doubleport (China)	> 0.990	distilled at reduced pressure	> 0.998	^{1}HNMR
$[C_3mim][HCO_3]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA,KF[b]
$[C_4mim][HCO_3]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_5mim][HCO_3]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_3mim][H_2PO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_4mim][H_2PO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_5mim][H_2PO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_2mmim][HSO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_3mmim][HSO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_4mmim][HSO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF
$[C_5mmim][HSO_4]$	synthesized		vacuum desiccation	> 0.990	^{1}HNMR, EA, KF

[a]Gas−liquid chromatography. [b]Karl Fischer titration.

Scheme 1. Synthesis Route of ILs



n=2, 3, 4, 5; R_1=CH_3 or H; X=HCO_3^-, $H_2PO_4^-$, HSO_4^-

(ET08, Mettler EasyPlus) was used to determine the water contents at atmospheric pressure. The water content of the ILs are listed in Table S8 (see Supporting Information). The contents of the residual Br^- were tested by $AgNO_3/HNO_3$ solution, and an approximately 50 ppm detection limit was found. It was estimated that the ILs' final purity was greater than 99% (mass percent). All determinations were performed under dry argon atmosphere in a glovebox. And the information on the synthesized ionic liquids were also listed in Table 2.

2.3. Measurements. *Density.* Mettler Toledo DM 45 density meter was used to measure ILs density (Mettler Toledo's vibrating U-tube technology under atmospheric pressure). Before performing the measurements, the density meter was calibrated with ultrapure dry air and water, and its reproducibility is 10^{-5} g·cm^{-3}.

Surface Tensions. A tensiometer (DPAW, Sang Li Electronic Co.) was used to measure the surface tensions by the forced bubble method. First, the surface tensions of ultrapure water (boiling and cooling) were measured in the temperature range 288.15−343.15 K and was in good agreement with the literature[24] within the experimental error of ±0.1 mN·m^{-1}. Then, the surface tension of the ILs were measured in the same condition. The temperature accuracy is 0.02 K.

Viscosity. The ILs' viscosity were measured at temperatures from (288.15 to 343.15) K using an Anton Paar SVM3000 viscometer which is based on a tube filled with the sample in a floats hollow measuring rotor. Calibration was performed using ultrapure water or viscosity standard oils (No. H117, Anton Paar Co.). The reproducibility of the viscosity measurements is 0.35%, the temperature accuracy is 0.02 K.

Electrical Conductivities. A Mettler Toledo SG3 conductivity meter, which operates with InLab738 conductivity probe (nominal 0.57 cm^{-1} ± 20% cell constant), was used to measure the electrical conductivities. The measurement frequency and voltage of the conduction were 50 Hz and 6 V, respectively. It was calibrated with the aqueous KCl solution under atmosphere pressure in the temperature range 288.15−343.15 K. The uncertainty in the measurements was ±5%. All values were listed in Table 3.

2.4. Calculations. Each 3D structure and energy of investigated ionic liquid complexes were calculated by Turbomole[25] through the COSMO-RS methodology[26] based on the DFT calculation. The function B3LYP and the TZVP basis set from the Turbomole library were both used.[27] All interaction energies were obtained under the supermolecular ansatz. The structural characteristics and the H-bond interactions were optimized and evaluated.

3. RESULTS AND DISCUSSION

The determination and comprehension of basic physicochemical and transport properties of ILs, such as density, viscosity, and conductivity are of great importance for equipment options and process design. The fundamental data about ILs may provide a better understanding of these ILs.[28]

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Table 3. Density, Surface Tension, Dynamics Viscosity, Electrical Conductivity, and Molar Conductivity of ILs at T = 288.15−343.15 K and 101 kPa[c]

T/K	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
	ρ/g·cm^{-3}											
[C_3mim][HCO_3]	1.17251	1.16904	1.16553	1.16201	1.1585	1.15499	1.15147	1.14795	1.14442	1.14087	1.13733	1.13377
[C_4mim][HCO_3]	1.16410	1.16050	1.15708	1.15364	1.15000	1.14651	1.14295	1.13945	1.13610	1.13253	1.12892	1.12552
[C_5mim][HCO_3]	1.14891	1.14521	1.14179	1.13828	1.13477	1.13133	1.12775	1.12428	1.12073	1.11727	1.11375	1.11030
[C_3mim][H_2PO_4]	1.20241	1.19896	1.19545	1.19195	1.18845	1.18495	1.18143	1.17789	1.17436	1.1708	1.16724	1.16366
[C_4mim][H_2PO_4]	1.18324	1.17991	1.17654	1.17318	1.16969	1.1663	1.1628	1.15953	1.15613	1.15267	1.14936	1.14603
[C_5mim][H_2PO_4]	1.14862	1.14542	1.14229	1.13909	1.13581	1.13255	1.12943	1.12627	1.12294	1.11993	1.11663	1.11349
[C_2mmim][HSO_4]	1.26194	1.25809	1.25443	1.25077	1.24708	1.2433	1.23959	1.2358	1.2322	1.22852	1.22482	1.22118
[C_3mmim][HSO_4]	1.23979	1.23623	1.23282	1.22924	1.22573	1.22213	1.21882	1.21529	1.21174	1.20835	1.20481	1.20146
[C_4mmim][HSO_4]	1.21709	1.21374	1.21061	1.20735	1.20389	1.20063	1.19749	1.19403	1.1908	1.18757	1.18429	1.18099
[C_5mmim][HSO_4]	1.19647	1.19323	1.19007	1.18689	1.18389	1.18069	1.17769	1.17461	1.17129	1.16833	1.16521	1.16218
	γ/mN·m^{-1}											
[C_3mim][HCO_3]	38.1	37.7	37.3	36.8	36.4	36.0	35.6	35.2	34.8	34.4	34.0	33.6
[C_4mim][HCO_3]	34.9	34.4	34.0	33.5	33.1	32.6	32.2	31.7	31.2	30.8	30.4	29.9
[C_5mim][HCO_3]	31.9	31.4	30.9	30.4	29.9	29.4	29.0	28.5	28.0	27.5	26.9	26.5
[C_3mim][H_2PO_4]	46.4	46.1	45.8	45.5	45.2	44.9	44.6	44.3	44	43.7	43.4	43.1
[C_4mim][H_2PO_4]	44.2	43.9	43.6	43.2	42.9	42.6	42.3	42	41.7	41.4	41.1	40.8
[C_5mim][H_2PO_4]	41.8	41.5	41.2	40.9	40.6	40.3	40	39.7	39.3	39	38.7	38.4
[C_2mmim][HSO_4]	50.4	50.1	49.8	49.5	49.3	49.0	48.7	48.4	48.1	47.8	47.5	47.2
[C_3mmim][HSO_4]	47.7	47.4	47.2	46.9	46.6	46.3	46.1	45.8	45.5	45.2	44.9	44.7
[C_4mmim][HSO_4]	45.3	45.0	44.8	44.5	44.2	43.9	43.7	43.4	43.1	42.8	42.6	42.3
[C_5mmim][HSO_4]	42.5	42.2	42.0	41.7	41.5	41.2	40.9	40.7	40.4	40.1	39.9	39.6
	η/mPa·s											
[C_3mim][HCO_3]	73.67	55.63	42.67	33.24	25.87	20.51	16.65	13.18	11.00	9.059	7.412	6.286
[C_4mim][HCO_3]	122.9	94.80	73.73	57.64	45.33	35.86	28.85	22.93	18.54	14.81	11.88	10.04
[C_5mim][HCO_3]	179.6	138.9	108.6	85.09	66.77	53.12	42.53	33.29	26.92	21.42	17.65	14.71
[C_3mim][H_2PO_4]	99.38	78.41	61.92	49.58	39.30	32.16	25.81	21.02	17.17	13.85	11.43	10.04
[C_4mim][H_2PO_4]	198.7	159.0	125.6	101.1	80.78	65.21	53.62	43.67	36.75	29.77	25.21	20.96
[C_5mim][H_2PO_4]	327.8	259.1	205.0	162.6	130.0	103.3	84.04	68.45	56.55	46.91	38.55	31.43
[C_2mmim][HSO_4]	375.0	263.6	186.0	134.9	98.41	72.94	53.72	40.12	30.20	22.37	17.96	12.57
[C_3mmim][HSO_4]	500.4	362.3	263.7	194.2	142.2	107.0	81.27	62.04	47.83	35.71	27.47	21.17
[C_4mmim][HSO_4]	628.5	469.7	355.2	271.3	206.3	157.2	121.8	95.86	74.49	60.70	46.52	38.13
[C_5mmim][HSO_4]	772.4	597.0	462.8	358.7	281.1	224.2	176.0	140.1	113.0	90.00	73.77	57.54
	σ/mS·cm^{-1}											
[C_3mim][HCO_3]	4.87	5.47	6.06	6.62	7.25	7.85	8.46	9.08	9.68	10.26	10.83	11.42
[C_4mim][HCO_3]	2.74	3.22	3.76	4.39	4.96	5.57	6.22	6.89	7.55	8.23	8.93	9.63

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Table 3. continued

T/K	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
	σ/mS·cm^{-1}											
[C_5mim][HCO_3]	1.43	1.93	2.48	3.05	3.67	4.28	4.89	5.53	6.12	6.71	7.33	7.94
[C_3mim][H_2PO_4]	4.69	5.36	6.13	6.93	7.85	8.79	9.77	10.82	11.86	13.02	14.12	15.46
[C_4mim][H_2PO_4]	3.03	3.59	4.19	4.83	5.55	6.28	7.07	7.88	8.68	9.65	10.59	11.59
[C_5mim][H_2PO_4]	1.64	2.01	2.43	2.9	3.41	3.98	4.57	5.23	5.88	6.65	7.44	8.25
[C_2mmim][HSO_4]			1.50	1.93	2.44	3.08	3.77	4.58	5.54	6.65	7.87	9.25
[C_3mmim][HSO_4]			1.23	1.62	2.11	2.67	3.33	4.09	4.96	6.00	7.11	8.32
[C_4mmim][HSO_4]			1.00	1.35	1.79	2.31	2.92	3.60	4.41	5.31	6.31	7.39
[C_5mmim][HSO_4]			0.75	1.05	1.45	1.97	2.57	3.24	3.99	4.85	5.73	6.75
	Λ/S·cm^2·mol^{-1}											
[C_3mim][HCO_3]	0.7734	0.87124	0.96814	1.0608	1.1653	1.2655	1.3680	1.4728	1.5750	1.6745	1.7731	1.8755
[C_4mim][HCO_3]	0.4713	0.5556	0.6507	0.7619	0.8636	0.9725	1.0894	1.2104	1.3303	1.4547	1.5830	1.7123
[C_5mim][HCO_3]	0.2666	0.3608	0.4650	0.5736	0.6923	0.8096	0.9278	1.0525	1.1683	1.2847	1.4075	1.5291
[C_3mim][H_2PO_4]	0.8624	0.9885	1.1338	1.2855	1.4605	1.6402	1.8285	2.0311	2.2330	2.4588	2.6747	2.9375
[C_4mim][H_2PO_4]	0.6021	0.7154	0.8373	0.9680	1.1156	1.2660	1.4296	1.5978	1.7652	1.9684	2.166	2.3778
[C_5mim][H_2PO_4]	0.3557	0.4372	0.5230	0.6343	0.7480	0.8755	1.0081	1.1569	1.3045	1.4793	1.6599	1.8458
[C_2mmim][HSO_4]			0.2658	0.3429	0.4348	0.5506	0.6759	0.8237	0.9992	1.2030	1.4281	1.6835
[C_3mmim][HSO_4]			0.2357	0.3114	0.4067	0.5162	0.6456	0.7952	0.9672	1.1732	1.3944	1.6362
[C_4mmim][HSO_4]			0.2068	0.2799	0.3722	0.4816	0.6104	0.7547	0.9270	1.1192	1.3337	1.5663
[C_5mmim][HSO_4]			0.1666	0.2338	0.3237	0.4410	0.5768	0.7291	0.9004	1.0973	1.2998	1.5352

[c]Standard uncertainties are $u(T) = 0.05$ K, $u(P) = 1$ kPa. The relative standard uncertainty is $u_r(\rho) = 0.002$; $u_r(\gamma) = 0.05$; $u_r(\eta) = 0.03$; $u_r(\sigma) = 0.05$.

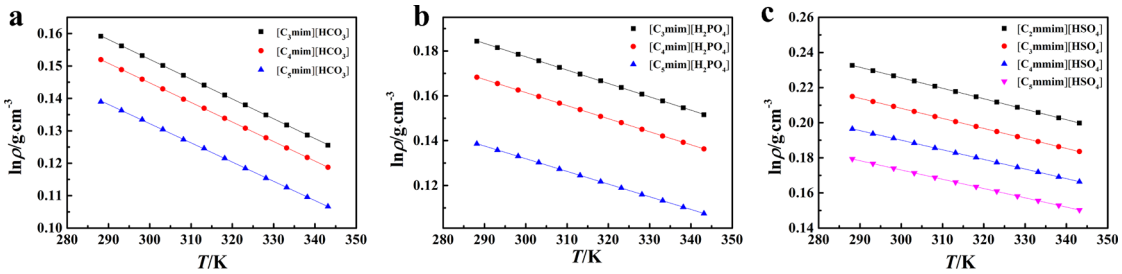

Figure 1. Linear fitting figure of ln ρ against T of ILs; (a) [C_{3-5}mim][HCO_3]; (b) [C_{3-5}mim][H_2PO_4]; (c) [C_{2-5}mmim][HSO_4].

3.1. Estimation of Volumetric Properties. Density is one of the important properties for the ILs. The density fluctuation can be reflected in the thermal properties of the ILs.[29] The temperature and alkyl spacer length of IL cation both have strong influences on density. It is found that when temperature increased, the density of all 10 kinds of ILs decreased, the density also decreased when the cation alkyl chain length increased, shown in Figure 1. These results are inconsistent with the results of imidazolium-based ILs with other anions;[30] the insufficient close packing of the cations may be responsible for these results. For the three series, the values of density are in the order [C_2mmim][HSO_4] > [C_3mmim][HSO_4] > [C_4mmim][HSO_4] > [C_5mmim][HSO_4]; [C_3mim][H_2PO_4] > [C_4mim][H_2PO_4] > [C_5mim][H_2PO_4]; [C_3mim][HCO_3] > [C_4mim][HCO_3] > [C_5mim][HCO_3]. The density of [C_4mmim][HSO_4] is 1.21374 g·cm^{-3}, which is close to [C_4mim][$MeSO_4$](1.2179g·cm^{-3}) with similar structure at 293.15 K.[31]

According to the least-squares method, the plots of ln ρ (density) vs T (temperature) were fitted by an empirical eq 1, and then straight lines can be obtained (Figure 1):

$$\ln \rho = a - bT \quad (1)$$

where a is an empirical constant, and thermal expansion coefficient is the negative value of the slope, $\alpha = -(\partial \ln \rho/\partial T)_p$. The values are listed in Table 4 and were found to be similar to

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Table 4. Estimated Values of Volumetric Properties of $[C_{3-5}mim][HCO_3]$, $[C_{3-5}mim][H_2PO_4]$ and $[C_{2-5}mmim][HSO_4]$ ILs at 298.15 K

ILs	$\alpha \times 10^{-4}$ / K^{-1}	V_m / nm^3	S^o / $J{\cdot}K^{-1}{\cdot}mol^{-1}$	U_{POT} / $kJ{\cdot}mol^{-1}$
$[C_3mim][HCO_3]$	6.1	0.2658	360.3	468.9
$[C_4mim][HCO_3]$	6.0	0.2875	387.8	459.3
$[C_5mim][HCO_3]$	5.9	0.3114	417.7	445.0
$[C_3mim][H_2PO_4]$	6.0	0.3072	412.5	451.5
$[C_4mim][H_2PO_4]$	5.8	0.3320	443.3	442.5
$[C_5mim][H_2PO_4]$	5.7	0.3623	481.1	432.9
$[C_2mmim][HSO_4]$	6.0	0.2943	396.4	456.6
$[C_3mmim][HSO_4]$	5.7	0.3184	426.4	447.4
$[C_4mmim][HSO_4]$	5.5	0.3435	457.6	438.9
$[C_5mmim][HSO_4]$	5.3	0.3690	489.4	430.9

those of common ILs.[32] That implies that the volume changes of the ILs with increasing temperature are greater than that of water and close to that of glycerinum.[33]

The molecular volume V_m of ILs at 298.15 K can be calculated from the experimental densities by the following equation and were listed in Table 4:

$$V_m = M{\cdot}(N{\cdot}\rho)^{-1} \quad (2)$$

where M is the molar mass and N is the Avogadro number.

By Glasser's theory,[34] standard entropy S^o can be estimated from a function of V_m at 298.15 K as follows:

$$S^o = 1246.5V_m + 29.5 \quad (3)$$

The standard entropy values calculated using eq 3 for ILs were listed in Table 4.

The lattice energy U_{POT} was also estimated by the Glasser theory[34] using the following equation at 298.15 K:

$$U_{POT} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (4)$$

The calculated lattice energies of the ILs were listed in Table 4. The lattice energies were found in the range 430.94−468.93 $kJ{\cdot}mol^{-1}$, which were close to those of a series of ILs $[C_{2-6}mim][BF_4]$.[35] All these results show that the lattice energies of the studied ILs are much lower than those of fused salts, for example, in all alkali halides, the fused CsI has the lowest lattice energy for 613 $kJ{\cdot}mol^{-1}$.[36] The low liquid state temperature of the ILs may result from the low lattice energy.

3.2. Estimation of Surface Properties. The surface tension values of the ILs were recorded and are shown in Table 3. From Figure 2, when the cation alkyl spacer length increased, the surface tension decreased, and it reflects the magnitude of the entropy increase associated with the surface assembling. The surface tension values of the ILs follow the order $[C_2mmim][HSO_4]$ > $[C_3mmim][HSO_4]$ > $[C_4mmim][HSO_4]$ > $[C_5mmim][HSO_4]$; $[C_3mim][H_2PO_4]$ > $[C_4mim][H_2PO_4]$ > $[C_5mim][H_2PO_4]$; $[C_3mim][HCO_3]$ > $[C_4mim][HCO_3]$ > $[C_5mim][HCO_3]$. The value of surface tension of $[C_5mmim][HSO_4]$ is 42.0 $mN{\cdot}m^{-1}$ at 298.15 K, close to the $[Smim][HSO_4]$ (37.5 $mN{\cdot}m^{-1}$, 298.15 K).[37]

The surface tensions of the studied ILs can be plotted by eq 5, and the values of surface tensions agree well with the values of refs 38 and 39.

$$\gamma/(mN{\cdot}m^{-1}) = a - bT \quad (5)$$

where the adjusted parameters a and b are obtained by the linear fitting, all the fitting linear correlation coefficients were >0.998. The surface excess entropy and surface excess energies were estimated from the surface tension using eq 6 (the slopes of eqs 5) and eq 7 at 298.15 K.

$$S_a = -b = -(\partial\gamma/\partial T)_p \quad (6)$$

$$E_a = \gamma - T(\partial\gamma/\partial T)_p \quad (7)$$

The estimated surface excess entropies and surface excess energies for the ILs were listed in Table 5.

Table 5. Surface Excess Entropy S_a, Surface Excess Energy E_a, and Enthalpy of Vaporization $\Delta_l{}^gH_m^0$ of ILs with Different Anions at 298.15 K

ILs	S_a / $mJ{\cdot}m^{-2}$	E_a / $mJ{\cdot}m^{-2}$	$\Delta_l{}^gH_m^0$ / $kJ{\cdot}mol^{-1}$
$[C_3mim][HCO_3]$	0.0819	61.7	106.2
$[C_4mim][HCO_3]$	0.0906	61.3	103.3
$[C_5mim][HCO_3]$	0.0981	60.7	98.3
$[C_3mim][H_2PO_4]$	0.0600	63.7	143.1
$[C_4mim][H_2PO_4]$	0.0619	62.1	143.5
$[C_5mim][H_2PO_4]$	0.0622	59.8	143.7
$[C_2mmim][HSO_4]$	0.0578	67.0	149.2
$[C_3mmim][HSO_4]$	0.0553	63.7	148.9
$[C_4mmim][HSO_4]$	0.0547	61.1	146.9
$[C_5mmim][HSO_4]$	0.0525	57.7	145.6

The enthalpy of vaporization $\Delta_l{}^gH_m^0$ (298.15 K) can be estimated from an empirical equation by Kabo et al.[40]

$$\Delta_l{}^gH_m^0 = A(\gamma V^{2/3}N^{1/3}) + B \quad (8)$$

where A and B are empirical parameters with values A = 0.01121 and B = 2.4 $kJ{\cdot}mol^{-1}$. The molar enthalpy of vaporization for the ILs was calculated from eq 8, and the results are presented in Table 5.

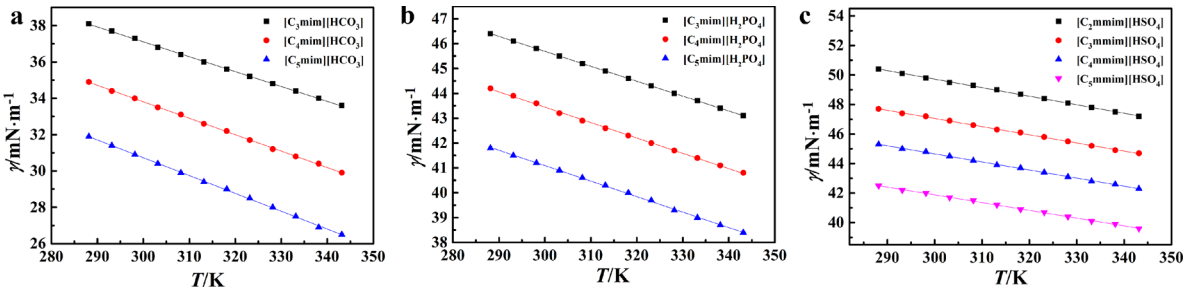

Figure 2. Surface tension as a function of temperature for ILs: (a) $[C_{3-5}mim][HCO_3]$; (b) $[C_{3-5}mim][H_2PO_4]$; (c) $[C_{2-5}mmim][HSO_4]$.

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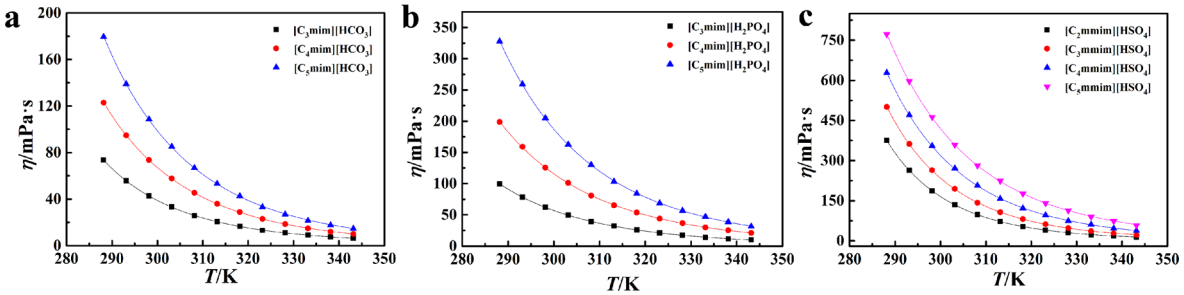

Figure 3. Dynamic viscosity as a function of temperature for ILs: (a) $[C_{3-5}mim][HCO_3]$; (b) $[C_{3-5}mim][H_2PO_4]$; (c) $[C_{2-5}mmim][HSO_4]$.

3.3. Dynamic Viscosity and Electrical Conductivity Characteristics. For ILs, viscosity and conductivity are important indications to the movement of electric charges and the transport capability. Further, information about the interactions between cations and anions are related to viscosity and electrical conductivity.[28]

The viscosity versus temperature data were tabulated in Table 3 and Figure 3; the viscosity of ILs were strongly impacted by the alkyl spacer length, and their viscosities are in the order $[C_2mmim][HSO_4]$ < $[C_3mmim][HSO_4]$ < $[C_4mmim][HSO_4]$ < $[C_5mmim][HSO_4]$; $[C_3mim][H_2PO_4]$ < $[C_4mim][H_2PO_4]$ < $[C_5mim][H_2PO_4]$; $[C_3mim][HCO_3]$ < $[C_4mim][HCO_3]$ < $[C_5mim][HCO_3]$. The viscosities of the ILs were increased with an alkyl spacer length increase, the potential reasons were increased vdW interaction between the alkyl groups. The viscosity value of $[C_4mmim][HSO_4]$ is 469.7 mPa·s (293.15 K), which is higher than the $[C_4mim][MeSO_4]$-(273.81 mPa·s, 293.15 K).[31]

The ionic liquids are usually called "fragile" liquids because their glassy structures can provoke a collapse with the thermal energy variations.[41] For our series of ILs, this energy change of fluidity can be properly expressed from viscosity by the VFT equation.

$$D = D_0 \exp(-E_D/(T - T_0)) \quad (9)$$

Figure 3 shows that the viscosity decreases with an increase in temperature by the VFT equation[42,43] (eq 9), the relationship between the temperature and viscosity of the ILs can be expressed as

$$\eta = \eta_0 \exp(-B/(T - T_0)) \quad (10)$$

where η_0, B, and T_0 are the adjustable constants. The fitted VFT parameters of ILs are listed in Table 6. The fitting correlation coefficients were all >0.9999, indicating that the VFT equation should be proper for describing the effect of temperature on the viscosities of the ILs.

The temperature dependence on conductivities of three series of ILs were shown as Figure 4. And the conductivities increase with an increase in temperature. The electric conductivity values are in the order $[C_2mmim][HSO_4]$ > $[C_3mmim][HSO_4]$ > $[C_4mmim][HSO_4]$ > $[C_5mmim]$-$[HSO_4]$; $[C_3mim][H_2PO_4]$ > $[C_4mim][H_2PO_4]$ > $[C_5mim]$-$[H_2PO_4]$; $[C_3mim][HCO_3]$ > $[C_4mim][HCO_3]$ > $[C_5mim]$-$[HCO_3]$. The highest electric conductivity observed for $[C_3mim][HCO_3]$, 6.06 mS·cm^{-1} (298.15 K), is close to that of the common IL $[C_4mim][SCN]$(4.56 mS·cm^{-1}, 298.15K).[23]

Further, the molar conductivity, Λ, was calculated on the basis of electric conductivity value based on the following equation:

Table 6. Fitted Parameter Values of VFT Equation of Dynamic Viscosity and Electrical Conductivity

ILs	D_0	E_D	T_0	$E\sigma/10^3$eV	R^2
		σ/mS·cm^{-1}			
$[C_3mim][HCO_3]$	56.4	252.4	185.1	21.7	0.99995
$[C_4mim][HCO_3]$	86.2	330.1	192.6	28.4	0.99995
$[C_5mim][HCO_3]$	36.2	157.9	239.3	13.6	0.99996
$[C_3mim][H_2PO_4]$	501.8	749.8	127.9	64.5	0.99990
$[C_4mim][H_2PO_4]$	296.5	612.0	154.5	52.6	0.99992
$[C_5mim][H_2PO_4]$	314.9	652.7	164.0	56.1	0.99996
$[C_2mmim][HSO_4]$	6463.1	1357.5	135.9	116.7	0.99997
$[C_3mmim][HSO_4]$	1703.4	904.8	173.1	77.8	0.99996
$[C_4mmim][HSO_4]$	715.9	675.5	195.4	58.1	0.99999
$[C_5mmim][HSO_4]$	237.6	416.6	226.2	35.8	0.99993
		Λ/S·cm^2·mol^{-1}			
$[C_3mim][HCO_3]$	10.8	285.7	179.6	24.6	0.99996
$[C_4mim][HCO_3]$	17.6	358.7	189.1	30.8	0.99995
$[C_5mim][HCO_3]$	7.5	168.5	237.7	14.5	0.99995
$[C_3mim][H_2PO_4]$	119.7	821.0	121.9	70.6	0.99991
$[C_4mim][H_2PO_4]$	73.1	661.4	150.2	56.9	0.99992
$[C_5mim][H_2PO_4]$	83.2	694.9	160.7	59.8	0.99996
$[C_2mmim][HSO_4]$	1459.3	1421.9	133.0	122.3	0.99997
$[C_3mmim][HSO_4]$	392.6	943.0	171.0	81.1	0.99996
$[C_4mmim][HSO_4]$	173.1	702.9	193.7	60.5	0.99999
$[C_5mmim][HSO_4]$	59.2	431.4	225.1	37.1	0.99993
		η/mPa·s			
	η_0	B	T_0	$E\eta/10^3$eV	R^2
$[C_3mim][HCO_3]$	9.2×10^{-4}	2.2×10^3	−91.5	190.9	0.99997
$[C_4mim][HCO_3]$	3.2×10^{-6}	5.8×10^3	41.3	495.4	0.99997
$[C_5mim][HCO_3]$	1.0×10^{-6}	6.9×10^3	74. 7	592.5	0.99993
$[C_3mim][H_2PO_4]$	4.0×10^{-6}	6.0×10^3	60.8	511.7	0.99992
$[C_4mim][H_2PO_4]$	2.1×10^{-5}	5.4×10^3	48.5	464.4	0.99988
$[C_5mim][H_2PO_4]$	1.4×10^{-5}	5.9×10^3	57.8	505.7	0.99992
$[C_2mmim][HSO_4]$	2.9×10^{-6}	4.8×10^3	−30.3	413.7	0.99995
$[C_3mmim][HSO_4]$	1.3×10^{-6}	5.9×10^3	7.5	503.1	0.99994
$[C_4mmim][HSO_4]$	3.4×10^{-6}	6.1×10^3	31.8	523.7	0.99993
$[C_5mmim][HSO_4]$	5.4×10^{-6}	6.6×10^3	62.7	566.7	0.99993

$$\Lambda = \sigma \cdot M \cdot \rho^{-1} \quad (11)$$

The Λ values of the ILs were listed in Table 3.

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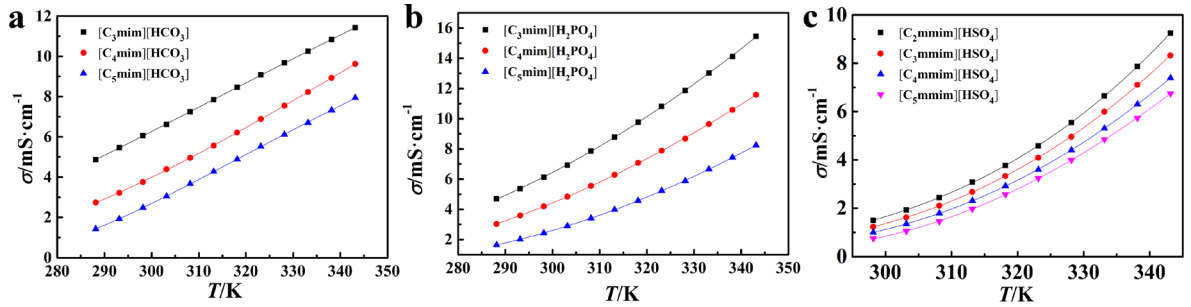

Figure 4. Electrical conductivity as a function of temperature for ILs: (a) $[C_{3-5}mim][HCO_3]$; (b) $[C_{3-5}mim][H_2PO_4]$; (c) $[C_{2-5}mmim][HSO_4]$.

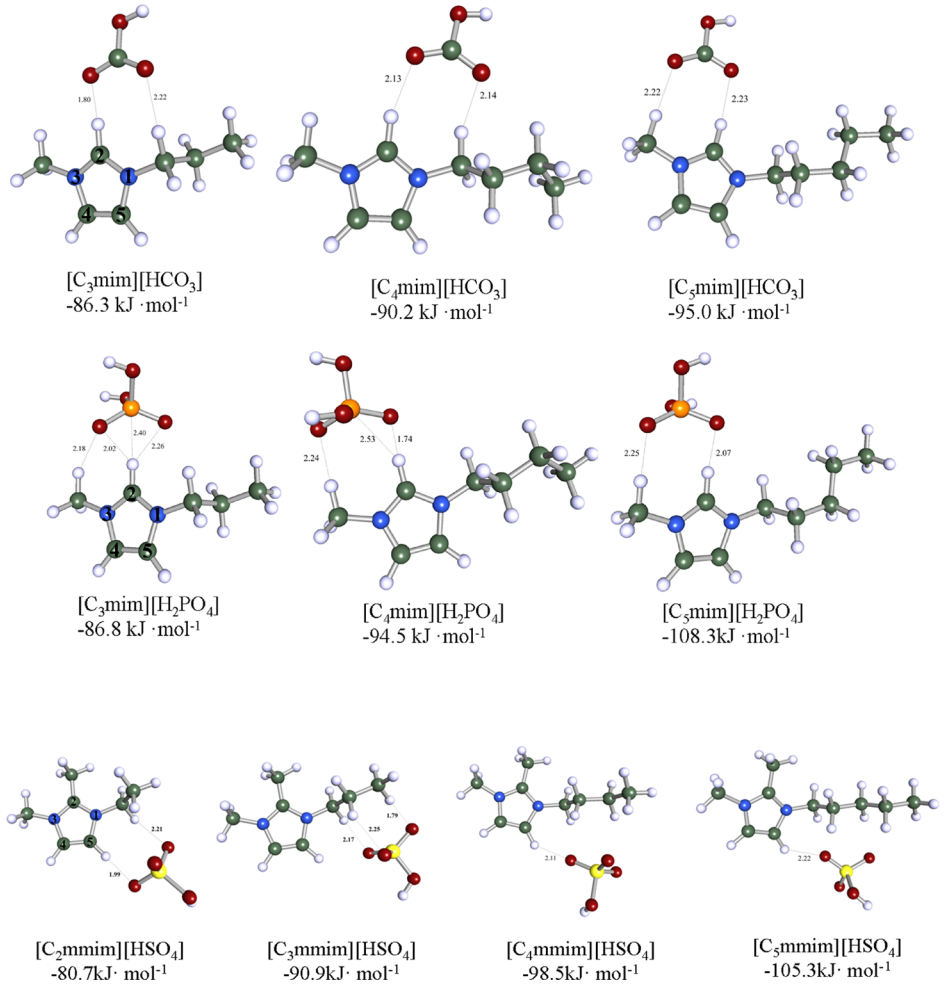

Figure 5. Optimized geometries, corresponding interaction energies, and the situation of hydrogen bonding of ILs. Atomic color corresponds to the element symbol: green, C; blue, N; white, H; red, O; orange, P; yellow, S.

The relationship between the conductivity, molar conductivity, and temperature of ILs can also be expressed by the VFT formula which is commonly used for the determination of conductivities of ILs:[43−45]

$$D = D_0 \exp(-E_D/(T - T_0)) \quad (12)$$

where D_0 and E_D are adjustable parameters and D is the conductivity or molar conductivity. The best fitted parameters of D_0, E_D, T_0, and the correlation coefficients R^2 were listed in Table 6.

Vila et al.[41] have established the fitting parameters of the VFT equation with Arrhenius equation: $\sigma_0 = \sigma_\infty$, $B = E_\sigma/k_B$. The final version of the VFT equation can be expressed as follows:

$$\sigma = \sigma_\infty \exp(-E_\sigma/(k_B(T - T_0)) \quad (13)$$

The activation energies of electrical conductivity for the ILs were calculated and listed in Table 6.

According to the discussion of Vila et al.,[41] the VFT equation for dynamic viscosity was also linked with the Arrhenius equation. The ultimate expression of the VFT formula displayed as follows:

$$\eta = \eta_\infty \cdot \exp(-E_\eta/(k_B(T - T_0)) \quad (14)$$

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Table 7. Interstice Parameters of ILs at 298.15 K

ILs	$\nu \cdot 10^{24}/cm^3$	$\sum\nu/cm^3$ (formula unit) $^{-1}$	$\alpha(cal) \cdot 10^{-4}/K^{-1}$	$\alpha(exp) \cdot 10^{-4}/K^{-1}$	$\sum\nu/V$ (%)
$[C_3mim][HCO_3]$	24.9	30.0	9.5	6.1	18.8
$[C_4mim][HCO_3]$	28.2	34.0	9.9	6.0	19.6
$[C_5mim][HCO_3]$	33.0	39.7	10.7	5.9	21.2
$[C_3mim][H_2PO_4]$	18.3	22.0	6.0	6.0	11.9
$[C_4mim][H_2PO_4]$	19.7	23.7	5.9	5.8	11.8
$[C_5mim][H_2PO_4]$	21.5	25.8	5.8	5.7	11.7
$[C_2mmim][HSO_4]$	23.7	28.5	8.0	6.0	16.1
$[C_3mmim][HSO_4]$	25.6	30.9	8.1	5.7	16.2
$[C_4mmim][HSO_4]$	28.3	34.0	8.3	5.5	16.5
$[C_5mmim][HSO_4]$	30.8	37.0	8.4	5.3	16.7

The activation energies of dynamic viscosity for the ILs were obtained from calculations and are listed in Table 6.

3.4. The Structural Effect and Interaction of Ionic Liquids. For a deep understanding of the structural effect of cation/anion on ILs properties, the DFT calculations are performed using Turbomole[25] following the COSMO-RS methodology.[26] The optimized structure, energy, and hydrogen bonds of these ionic liquids are obtained (see Figure 5). The main differences of structure between these three series of ILs are the alkyl chain, the vicinal methyl on the imidazolium ring, and the species of anion, respectively. The interactions between anions and cations will influence the physicochemical properties inevitably. Ions of these AILs interact via hydrogen bond (HB) forces, vdW forces, and Coulombic, as we know, thus forming directional bonding between the constituent ions.[10]

The 2.5 Å of sum vdW atomic radii of hydrogen and oxygen is used as a critical value for determining the existence of a hydrogen bond between hydrogen and oxygen atoms.[46] Dashed lines are utilized for representing hydrogen bonds, and the the labeled H···O distances are seen in Figure 5. It is found that hydrogen bonds can exist between C2−H or methyl C−H of cations and O atom of anions for the ILs with $[HCO_3]$, $[H_2PO_4]$, and $[HSO_4]$ anions. The C2−H is usually the most active atom for dialkylimidazolium ILs.[27] And for the $[C_nmmim][HSO_4]$, due to the vicinal methyl on the imidazolium ring, the H-bonding interaction occurs on the position of C4,5−H. It is shown that the numbers of H-bonds between the ion pairs are different (Figure 5); however, this has no evident influence on the total interaction energy, which indicates that the Coulombic interaction between the cations and anions of these ILs is dominant.

The higher viscosities may be impacted by the ion−ion interaction, vdW interaction, or electrostatic attraction, and the electrical conductivity usually has an opposite tendency.[28]

3.5. Interstice Model for the Ionic Liquids. To date, several theories have been put forward to describe the structural and transport properties of pure ILs.[47−50] Herein, for the ours families ionic liquids, a simpler interstice model is employed to estimate.[51−53]

The interstice volume ν can be obtained based on the classical statistical mechanics as represented by the following equation:

$$\upsilon = 0.6791(k_bT/\gamma)^{3/2} \tag{15}$$

where k_b is the Boltzmann's constant, and the ν values of the ILs were listed in Table 7.

The molar volume of ILs, V, consists of the inherent volume, V_i, and the total volume of the all interstices $\sum\nu = 2N\nu$, that is

$$V = 2N\nu + V_i \tag{16}$$

If the expansion of ILs entirely caused by the expansion of the interstices along with temperature increases, the coefficient α can be calculated based on the interstice model:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{3N\nu}{VT} \tag{17}$$

According to the interstice model, all the correlation parameters of the ILs at 298.15 K are estimated and listed in Table 6. Typically, the $\sum\nu/V$ are close to 10% to 15% for a volume change from ion solid to melt, and the results of the studied ILs are very close to the empirical regularities.

The acid radical will form some small interstice in the structure, while the interstice theory considers that the interstice between the anion and cation is bubble, so the deviation of the thermal expansion coefficients may be larger, but still within an order of magnitude. Thus, the interstice theory can also possibly estimate the qualitative nature of voids.

A comparison of the thermal expansion coefficients $\alpha(exp)$ and $\alpha(cal)$ obtained from experimental and calculated data shows that most of the deviations are about 10−15%, which shows that the interstice model parameters of these ILs were reasonable.

4. CONCLUSION

In this work, we have prepared and characterized 10 kinds of ionic liquids: $[C_{3-5}mim][HCO_3]$, $[C_{3-5}mim][H_2PO_4]$, and $[C_{2-5}mmim][HSO_4]$. The physicochemical properties of the ionic liquids such as density, viscosity, surface tension, and electrical conductivity were measured and thermodynamic parameters were estimated from the experimental data by empiric or semiempiric methods. Then, according to the VFT equation, the temperature dependences of the ILs viscosities and electrical conductivities were described graphically. Furthermore, by DFT calculations, the structural effects from the vicinal methyl and the alkyl chain length on the ILs properties were discussed based on the interactions between cations and anions. It was found that the Coulombic interaction between cation and anion is dominant for these ILs. The interstice model of the ILs was applied to evaluate the internal structure change of ILs, and the interstice parameters were estimated. The results showed that the interstice model could be appropriately applied to these 10 ILs with three types of anions.

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■ ASSOCIATED CONTENT

Supporting Information

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FTIR, ^{1}HNMR spectra, and EA for ILs in this work (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangqingguo@bhu.edu.cn. Tel.: +86 18641695401. Fax: +86 416 3400310.

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Notes

The authors declare no competing financial interest.

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